DOCUMENT-IDENTIFIER: US 20020006576 A1

TITLE: Positive type photoresist composition

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Detail Description Paragraph - DETX (51):

[0241] Coefficient of Variation in Sensitivity: The coefficient of variation in sensitivity was evaluated from the viewpoint of aging stability. A solution of the positive type photoresist composition prepared was stored at 30.degree. C. for 1 month. Then, it was applied onto a silicon wafer and exposed in the same manner as above. The relative sensitivity was determined, and the difference from the above-mentioned relative sensitivity before storage was determined as the coefficient of variation with time.

US 20020006576A1

(19) United States
(12) Patent Application Publication (10) Pub. No.: US 2002/0006576 A1
Sato et al. (43) Pub. Date: Jan. 17, 2002

(54) POSITIVE TYPE PHOTORESIST COMPOSITION

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(21) Appl. No.: 09/728,853

(22) Filed: Dec. 6, 2000

Related U.S. Application Data

(63) Continuation of application No. 08/023,602, filed on Feb. 12, 1998, now Pat. No. 5,214,517.

(30) Foreign Application Priority Data

Feb. 17, 1997 (JP) ..... HEI. 9-32431
Feb. 27, 1997 (JP) ..... HEI. 9-43874
Mar. 3, 1997 (JP) ..... HEI. 9-48055
Mar. 7, 1997 (JP) ..... HEI. 9-52583

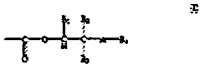
Publication Classification

(51) Int. Cl.[7] G03F 7/039

(52) U.S. Cl. 430/270.1

(57) ABSTRACT

A positive type photoresist composition suitable for light in the wavelength region of 170 nm to 220 nm, high in sensitivity, excellent in adhesion and giving a good resist pattern profile, which comprises a resin having an acetal group represented by the following general formula [I] in its molecule and a compound generating an acid by irradiation of an active light ray or radiation:



wherein R_1 represents a hydrogen atom, an alkyl group or a cycloalkyl group, and R_2 and R_{2a} which may be the same or different, each represents a hydrogen atom, an alkyl group, a cycloalkyl group or -A-R_{3a}, and R_3 and R_1 may combine together to form a ring, wherein R_3 represents a hydrogen atom, an alkyl group or a cycloalkyl group, R_4 and R_5 or R_6 may combine together to form a ring, and A represents an oxygen atom or a sulfur atom.

US-PAT-NO: 6432616

DOCUMENT-IDENTIFIER: US 6432616 B1

TITLE: Water soluble polymer and photoresist composition containing the same

---------- KWIC ---------

Detailed Description Text - DETX (9):

After the photoresist was stored for three months, the above-mentioned exposure evaluation was repeated. It was found that neither the resolution nor adhesion changed.

US006432616B1

(12) **United States Patent**
Song et al.

(10) Patent No.: **US 6,432,616 B1**
(45) Date of Patent: **Aug. 13, 2002**

(54) WATER SOLUBLE POLYMER AND PHOTORESIST COMPOSITION CONTAINING THE SAME

(75) Inventors: [illegible]-Tang Song, Taipei; [illegible]-Jiin Yang, Tao-Yuan; [illegible]-Mei Chen; Yi-Hau Lin, both of Hsinchu, all of (TW)

(73) Assignee: Industrial Technology Research Institute, Hsinchu (TW)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: 09/634,473

(22) Filed: Aug. 7, 2000

(30) Foreign Application Priority Data

Dec. 17, 1999 (TW) .... 88122229 A

(51) Int. Cl.[7] G03C 1/73; C08F 8/30; C08F 8/34; C08F 8/40; C08F 2/46

(52) U.S. Cl. 430/281.1; 430/281.1; 430/270.1; 430/905; 430/916; 525/329.5; 525/330.1; 525/363; 525/385; 522/65; 522/37; 522/40; 522/43; 522/46; 522/39; 522/53

(58) Field of Search 525/329.5, 330.1, 525/363, 385; 522/65, 37, 40, 43, 46, 39, 53; 430/287.1, 285.1, 916, 905, 916, 270.1, 281.1

(56) References Cited

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Primary Examiner—Janet Baxter
Assistant Examiner—Sin J. Lee
(74) *Attorney, Agent, or Firm*—Darby & Darby

(57) ABSTRACT

The present invention provides a water soluble polymer which is prepared by the following steps. First, a carboxyl group-containing polymer is reacted with an alkaline reagent so that a portion of the carboxyl groups are reacted in an amount sufficient to make the polymer water soluble. Then, the polymer obtained is reacted with an epoxide containing unsaturated bonds and/or heteroatoms so that 1 to 100 mole percent of the remaining carboxyl groups of the polymer are reacted with the epoxide to form ester groups via a ring-opening reaction of epoxides, wherein the heteroatom can be silicon, nitrogen, phosphorus or sulfur. The water soluble polymer of the present invention can be used as a photosensitive resin. When the photoresist composition is used for preparing printed circuit boards, it exhibits high photosensitivity, good water dispersability, storage stability, and good adhesion to copper. In addition, the problem of sticking to the mask can be prevented.

13 Claims, No Drawings

US-PAT-NO: 6372406

DOCUMENT-IDENTIFIER: US 6372406 B1

TITLE: Deactivated aromatic amines as additives in acid-catalyzed resists

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Detailed Description Paragraph Table - DETL (2):

E.sub.0 The photoresist stored at 0.degree. C. for 15 days: 6.6 mJ/cm.sup.2 The photoresist stored at 40.degree. C. for 15 days: 5.2 mJ/cm.sup.2 (Change: 21%)

Detailed Description Paragraph Table - DETL (4):

E.sub.0 The photoresist stored at 0.degree. C. for 15 days: 4.8 mJ/cm.sup.2 The photoresist stored at 40.degree. C. for 15 days: 4.2 mJ/cm.sup.2 (Change: 12.5%)

Detailed Description Paragraph Table - DETL (6):

E.sub.0 The photoresist stored at 0.degree. C. for 15 days: 9.0 mJ/cm.sup.2 The photoresist stored at 40.degree. C. for 15 days: 9.0 mJ/cm.sup.2 (Change: 0%)

US006372406B1

(12) **United States Patent**
Brunsvold et al.

(10) Patent No.: US 6,372,406 B1
(45) Date of Patent: Apr. 16, 2002

(54) **DEACTIVATED AROMATIC AMINES AS ADDITIVES IN ACID-CATALYZED RESISTS**

(75) Inventors: William R. Brunsvold; Ahmad D. Katnani; Pushkara R. Varanasi, all of Poughkeepsie, NY (US)

(73) Assignee: International Business Machines Corporation, Armonk, NY (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: 09/706,682

(22) Filed: Nov. 6, 2000

Related U.S. Application Data

(63) Continuation of application No. 09/148,868, filed on Sep. 3, 1998.

(51) Int. Cl.[7] G03C 1/73

(52) U.S. Cl. 430/270.1; 430/281.1; 430/325; 430/914; 430/919; 430/920; 430/921; 430/923

(58) Field of Search 430/270.1, 914, 430/326, 919, 922, 921, 923, 281.1

(56) References Cited

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Primary Examiner—Janet Baxter
Assistant Examiner—Sin J. Lee
(74) *Attorney, Agent, or Firm*—Steven Capella

(57) **ABSTRACT**

Deactivated aromatic amines are useful to improve shelf life and performance of acid-catalyzed photoresist compositions without adverse interaction with radiation-sensitive acid generator components in said resist. The compositions are especially useful in photolithography processes used in forming integrated circuits and other miniaturized components.

6 Claims, No Drawings

US-PAT-NO: 6127074

DOCUMENT-IDENTIFIER: US 6127074 A

TITLE: Photoresist solution for phosphor slurry applied to color cathode ray tube

---------- KWIC ---------

Brief Summary Text - BSTX (40):

Also the photoresist solution can be stored for a long time without change of properties thereof since the initiator does not decompose Diazo photosensitizer.

US006127074A

United States Patent [19]
You et al.

[11] Patent Number: 6,127,074
[45] Date of Patent: Oct. 3, 2000

[54] **PHOTORESIST SOLUTION FOR PHOSPHOR SLURRY APPLIED TO COLOR CATHODE RAY TUBE**

[75] Inventors: Seung-Jae Yoo, Kyunggi-do; Eak-Cheol Eum, Kyunggi-do; Young-Jong Kang, Seoul; Chang-Wook Kim, Gi-Wook Kang, both of Kyunggi-do; Eun-Ha Han, Seoul, all of Rep. of Korea

[73] Assignee: Samsung Display Devices Co., Ltd., Rep. of Korea

[21] Appl. No.: 09/209,234

[22] Filed: Dec. 11, 1998

[30] Foreign Application Priority Data

Dec. 30, 1997 [KR] Rep. of Korea 97-79283
Nov. 6, 1998 [KR] Rep. of Korea 98-47455

[51] Int. Cl.[7] G03C 5/00; G03F 7/021; G03F 7/012

[52] U.S. Cl. 430/28, 430/175; 430/156; 430/197

[58] Field of Search 430/7, 23, 28, 430/175, 196, 197

[56] References Cited

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Primary Examiner—John S. Chu
Attorney, Agent, or Firm—Baker & McKenzie

[57] **ABSTRACT**

The present invention relates to photoresist solution for phosphor slurry for use in the color cathode ray tube. The photoresist solution of the present invention comprises Diazo or Bisazide photosensitizer, polymer, which is mixed with said Diazo or Bisazide photosensitizer, obtained by polymerization of hydroxy ethyl acrylate base. The photoresist solution of the present invention improves the adhesive strength by using of the Diazo or Bisazide photosensitizer and the polymer, thus the grass, line and end phosphor screen being uniformly formed and the color residue being disappeared. Further, since the photosensitizer not containing heavy metal is used, it does not cause any environmental problem. Also, it can be stored for a long time by using the initiator without hydrochloric acid at the time of polymerization.

12 Claims, No Drawings

Detail Description Paragraph - DETX (17):

[0057] A solution of a base resin for the photoresist composition was prepared by dissolving, in 400 parts of propyleneglycol monomethyl ether acetate, 50 parts of the same first partially 1-ethoxyethyl-substituted polyhydroxystyrene resin as used in Reference Example 3 and 50 parts of a second partially substituted polyhydroxystyrene resin of which 25% of the hydroxyl groups were substituted by 1-ethoxyethyl groups, having a weight-average molecular weight of 5000 with a molecular weight dispersion of 1.2 and exhibiting a dissolving velocity of 150 nm/minute in a 2.38% by weight aqueous solution of tetramethylammonium hydroxide.

Detail Description Paragraph - DETX (18):

[0058] A coating layer formed on a silicon wafer by coating with the above prepared solution of the base resin combination followed by drying exhibited a dissolving velocity of 40 nm/minute under the same testing conditions.

Detail Description Paragraph - DETX (20):

[0059] A positive -working photoresist compositin was prepared by dissolving, in 490 parts of propyleneglycol monomethyl ether acetate, 30 parts of the same combination of the two partially tert-butoxycarbonyl-substituted resins as in Reference Example 1, 70 parts of the same combination of the two partially 1-ethoxyethyl-substituted resins as in Reference Example 3, 7 parts of bis(cyclohexylsulfonyl) diazomethane, 0.1 part of triethylamine and 0.5 part of salicylic acid followed by filtration of the solution through a membrane filter of 0.2 .mu.m pore diameter.

Detail Description Paragraph - DETX (21):

[0060] This positive -working photoresist composition was subjected to the evaluation tests of the above described testing items (1) to (5) to obtain results including:

Detail Description Paragraph - DETX (28):

[0066] The formulation of the positive -working photoresist composition and the

US 20020110750A1

(19) United States
(12) Patent Application Publication (10) Pub. No.: US 2002/0110750 A1
Sato et al. (43) Pub. Date: Aug. 15, 2002

(54) POSITIVE-WORKING PHOTORESIST COMPOSITION

(75) Inventors: Kazuhisa Sato, Sagamihara-shi (JP); Satoshi Maezawa, Sagamihara-shi (JP); Taku Nakao, Fujisawa-shi (JP); Kazuyuki Nitta, Ebina-shi (JP)

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WASHINGTON, DC 20006-1021 (US)

(21) Appl. No.: 10/114,258

(22) Filed: Apr. 3, 2002

Related U.S. Application Data

(62) Division of application No. 09/521,305, filed on Mar. 8, 2000.

(30) Foreign Application Priority Data

Mar. 18, 1999 (JP) 11-74097

Publication Classification

(51) Int. Cl.[7] G03F 7/039
(52) U.S. Cl. 430/270.1; 430/905; 430/326; 430/325

(57) ABSTRACT

Disclosed is a novel chemical-amplification positive-working photoresist composition capable of giving a patterned resist layer with excellent properties such as photosensitivity, pattern resolution, heat resistance and cross sectional profile of the patterned resist layer. The composition is characterized by the use of, as the film-forming resinous component, a hydroxyl-containing resinous ingredient which is a combination of a first resin of which from 30 to 50% of the hydroxyl groups are substituted by acid-dissociable solubility-reducing groups and a second resin of which from 5 to 20% of the hydroxyl groups are substituted by acid-dissociable groups of the same kind as in the first resin in a weight proportion of 1:9 to 9:1.

to 0.22 .mu.m and a cross sectional profile of good orthogonality.

Summary of Invention Paragraph - BSTX (47):

[0044] In the following, the positive -working chemical-amplification photoresist composition of the present invention is described in more detail by way of Examples. In the following description, the term of "parts" always refers to "parts by weight".

Detail Description Paragraph - DETX (2):

[0045] A positive -working photoresist composition was prepared by uniformly dissolving, in 800 parts of propyleneglycol monoethyl ether acetate,

Detail Description Paragraph - DETX (3):

[0046] 60 parts of a first copolymeric resin, referred to as the resin I hereinafter, having a weight-average molecular weight of 10,000 and consisting of 65% by moles of hydroxystyrene units, 20% by moles of styrene units and 15% by moles of tert-butyl acrylate units,

Detail Description Paragraph - DETX (4):

[0047] 40 parts of a second copolymeric resin, referred to as the resin II hereinafter, having a weight-average molecular weight of 10,000 and consisting of 65% by moles of hydroxystyrene units, 30% by moles of styrene units and 5% by moles of tert-butyl acrylate units,

Detail Description Paragraph - DETX (7):

[0050] 0.5 part of salicylic acid,

Detail Description Paragraph - DETX (9):

[0052] A semiconductor silicon wafer of 6 inches diameter after a treatment with hexamethyl disilazane was coated on a spinner with the above prepared photoresist solution followed by drying under heating on a hot plate at 130.degree. C. for 90 seconds to give a dried photoresist layer having a

...tert-butyl acrylate units,

[0048] 3 parts of bis(4-tert-butylphenyl) iodonium nonafluorobutane sulfonate,

[0049] 0.5 part of triethanolamine, and

[0050] 0.5 part of salicylic acid,

0051] followed by filtration of the solution through a membrane filter of 0.2 μm pore diameter.

0052] A semiconductor silicon wafer of 6 inches diameter er a treatment with hexamethyl disilazane was coated on spinner with the above prepared photoresist solution lowed by drying under heating on a hot plate at 130° C. 90 seconds to give a dried photoresist layer having a ckness of 0.7 μm. In the next place, the photoresist layer s exposed pattern-wise to a KrF excimer laser beam on a nifying projection exposure machine (Model FPA-00EX3, manufactured by Canon Co.) followed by a st-exposure baking treatment at 120° C. for 90 seconds d then by a puddle development treatment at 23° C. for 65 conds in a 2.38% by weight aqueous solution of tetram-ylammonium hydroxide to give a positively patterned ist layer.

0053] A fully resolved line-and-space pattern of 0.22 μm e width could be obtained in this way. The thus patterned ist lines had an excellently orthogonal cross sectional ofile standing upright on the substrate surface. The mini-im exposure dose for obtaining the line-and-space resist ttern of 0.22 μm width was 30 mJ/cm² as a measure of the otosensitivity. The critical pattern resolution was 0.19 μm.

COMPARATIVE EXAMPLE 1

0054] The experimental procedure was substantially the me as in Example 1 excepting for modification of the mulation of the photoresist composition by replacing mbination of 60 parts of the resin I and 40 parts of the in II with 100 parts of a third copolymeric resin having a ight-average molecular weight of 10,000 and consisting 55% by moles of hydroxystyrene units, 20% by moles of rene units and 25% by moles of tert-butyl acrylate units.

0055] The results of the evaluation tests of the patterned ist layer were that line-and-space patterns of a line width aller than 0.25 μm could not be obtained and the cross tional profile of a line-patterned resist layer of 0.25 μm dth was trapezoidal. The minimum exposure dose for taining the line-and-space pattern of 0.25 μm line width s 30 mJ/cm².

COMPARATIVE EXAMPLE 2

0056] The experimental procedure was substantially the me as in Example 1 excepting for modification of the mulation of the photoresist composition by replacing (4-tert-butyl-phenyl) iodonium nonafluorobutane sul-

EXAMPLE 2

[0058] The experimental procedure was substa same as in Example 1 excepting for modificati formulation of the photoresist composition by inc amount of the resin I from 60 parts to 80 parts, the amount of the resin II from 40 parts to 20 additional admixture of the composition with dimethylacetamide and for an increase of the pre baking temperature and post-exposure baking te from 130° C. to 140° C. and from 120° C. to respectively.

[0059] The results of the evaluation tests of the resist layer were that a hole pattern of 0.20 μm could be obtained in this way. The thus formed h had an excellent cross sectional profile perpe reaching the substrate surface. The minimum exp for obtaining the hole pattern of 0.20 μm diame mJ/cm² as a measure of the photosensitivity. T pattern resolution was 0.19 μm.

COMPARATIVE EXAMPLE 3

[0060] The experimental procedure was substa same as in Example 2 excepting for modificati formulation of the photoresist composition by re combination of 80 parts of the resin I and 20 p resin II with 100 parts of the third copolymeric re in Comparative Example 1.

[0061] The results of the evaluation tests of the resist layer were that hole patterns of 0.30 μm d finer could not be obtained and the sensitivity for a 0.30 μm hole pattern was 40 mJ/cm².

COMPARATIVE EXAMPLE 4

[0062] The experimental procedure was substa same as in Example 2 excepting for modificati formulation of the photoresist composition by bis(4-tert-butyl-phenyl) iodonium nonafluorobu fonate with the same amount of triphenylsulfoni romethane sulfonate.

[0063] The results of the evaluation tests of the resist layer were that hole patterns of 0.22 μm d finer could not be obtained and the sensitivity for a 0.22 μm hole pattern, i.e. the minimum exposure 40 mJ/cm², although the cross sectional profile pattern was good perpendicularly reaching the surface.

What is claimed is:

1. A positive-working chemical-amplification composition which comprises, as a uniform solu organic solvent:

patterned resist layer and stability of the latent images before development, that the photoresist composition further contains an aliphatic tertiary amine compound as a component (C). Examples of preferable aliphatic tertiary amine compounds include trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, triethanolamine, tributanol amine and the like, of which triethanolamine is particularly preferable although any of these amine compounds can be used either singly or as a combination of two kinds or more according to need.

Detailed Description Text - DETX (13):

While additional addition of the above mentioned amine compound to the inventive photoresist composition may eventually have a disadvantageous effect of decreasing the photosensitivity of the composition, this disadvantage can be overcome, along with a beneficial effect of improving the pattern resolution, by the admixture of a carboxylic acid as a component (D) in combination with the component (C). Preferable carboxylic acids suitable for this purpose include aliphatic saturated dicarboxylic acids and aromatic carboxylic acids.

Detailed Description Text - DETX (14):

Examples of suitable aliphatic saturated dicarboxylic acids include oxalic, malonic, succinic and glutaric acids. Examples of suitable aromatic carboxylic acids include aromatic mono- and polycarboxylic acids having a hydroxyl or nitro group as a substituent group such as 2-hydroxy benzoic acid, 4-hydroxy benzoic acid, 2-hydroxy-3-nitro benzoic acid, 3,5-dinitro benzoic acid, 2-nitro benzoic acid, 2,4-dihydroxy benzoic acid, 2,5-dihydroxy benzoic acid, 2,6-dihydroxy benzoic acid, 3,4-dihydroxy benzoic acid, 3,5-dihydroxy benzoic acid, 2-vinyl benzoic acid, 4-vinyl benzoic acid, phthalic acid, terephthalic acid and isophthalic acid. These carboxylic acids can be used either singly or as a combination of two kinds or more according to need. Among the above named carboxylic acids, 2-hydroxy benzoic acid, i.e. salicylic acid, and malonic acid are particularly preferable.

Detailed Description Text - DETX (15):

As to the amount of the optional component (C) in the inventive photoresist composition, the amine compound is added to the composition in an amount in the range from 0.001 to 10 parts by weight or, preferably, from 0.01 to 1.0 part by weight per 100 parts by weight of the component (A) in consideration of orthogonality of the cross sectional profile of the resist pattern, stability of the latent images before development and photo sensitivity of the composition

Detailed Description Text - DETX (16):

The amount of the carboxylic acid as the component (D), when added to the inventive photoresist composition, is in the range from 0.001 to 10 parts by weight or, preferably, from 0.01 to 1.0 part by weight per 100 parts by weight of the component (A). Addition of the component (D) to the inventive photoresist composition has an effect of preventing a decrease in the photosensitivity of the composition as a side effect of the component (C) along with further improvement of orthogonality of the cross sectional profile of the patterned resist layer.

layer by a development manner in the unexposed areas to give a patterned resist layer having an excellently orthogonal cross sectional profile.

As the inventive photoresist composition comprising the copolymeric resinous ingredient as the component (A), which can be either one or a combination of two kinds or more of copolymeric resins falling within the definition of the above described ternary copolymeric resins, it is preferable that the component (A) is a combination of a first copolymeric resin (A1) consisting of from 62 to 68% by moles of the monomeric units of the first class (a), from 15 to 35% by moles of the monomeric units of the second class (b) and from 12 to 18% by moles of the monomeric units of the third class (c) and a second copolymeric resin (A2) consisting of from 62 to 68% by moles of the monomeric units of the first class (a), from 25 to 35% by moles of the monomeric units of the second class (b) and from 2 to 8% by moles of the monomeric units of the third class (c) in a weight proportion in the range from 9:1 to 5:5 or, preferably, from 8:2 to 6:4 in respect of the superiority in the photosensitivity, pattern resolution and orthogonality of the cross sectional profile of the patterned resist layer.

It is preferable that the copolymeric resin as the component (A) has a weight-average molecular weight in the range from 3000 to 30000 as determined by the gel permeation chromatographic (GPC) method by making reference to known polystyrene resins. When the weight-average molecular weight of the component (A) is too low, the photoresist composition cannot be fully film-forming while, when the weight-average molecular weight of the resin is too high, the resin cannot be fully soluble in an aqueous alkaline solution.

The component (B) contained in the inventive photoresist composition in combination with the above described component (A) is a radiation-sensitive acid-generating agent which is a compound capable of releasing an acid by decomposition under irradiation with actinic rays such as ultraviolet light. The acid-generating agent in the inventive photoresist composition is not particularly limitative and can be selected from known ones. It is preferably an onium salt compound containing a fluoroalkyl sulfonate ion of 1 to 10 carbon atoms as the anion.

The cation in the onium ion of the above mentioned onium salt compound is not particularly limitative and can be selected from known ones. Suitable cations include, for example, phenyl iodonium and sulfonium ions which may optionally be substituted by a lower alkyl group such as methyl, ethyl, propyl, n-butyl and tert-butyl groups or a lower alkoxy group such as methoxy and ethoxy groups.

On the other hand, the anion of the onium salt compound is a fluoroalkyl sulfonate ion obtained by substituting fluorine atoms for a part or all of the hydrogen atoms in an alkyl group of 1 to 10 carbon atoms. It is preferable that the alkyl group in the fluoroalkyl sulfonate ion has 1 to 5 carbon atoms and all of the hydrogen atoms thereof are replaced with fluorine atoms since the acid strength of the sulfonate ion as a sulfonic acid is decreased as the chain length of the alkyl group is increased and the degree of fluorination of the alkyl group is decreased.

Particular examples of the onium salt compounds suitable as the component (B) in the inventive photoresist composition include diphenyl iodonium trifluoromethane or nonafluorobutane sulfonate, bis(4-tert-butylphenyl) iodonium trifluoromethane or nonafluorobutane sulfonate, triphenyl sulfonium trifluoromethane or nonafluorobutane sulfonate and tri(4-methylphenyl) sulfonium trifluoromethane or nonafluorobutane sulfonate. Any of the above named onium salt compounds can be used either singly or as a combination of two kinds or more according to need.

The amount of the onium salt compound as the component (B) in the inventive photoresist composition is in the range from 1 to 20 parts by weight per 100 parts by weight of the component (A). When the amount of the component (B) is too small, good pattern formation can hardly be accomplished while, when the amount of the component (B) is too large, a photoresist composition in the form of a uniform solution cannet be obtained due to the limited solubility of the component in an organic solvent to cause a decrease in storage stability of the photoresist solution.

While the essential ingredients in the inventive photoresist composition are the above described components (A) and (B), it is optional, if necessary with an object to improve orthogonality of the cross sectional profile of the patterned resist layer and stability of the latent images before development, that the photoresist composition further contains an aliphatic tertiary amine compound as a component (C). Examples of preferable aliphatic tertiary amine compounds include trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, triethanolamine, tributanol amine and the like, of which triethanolamine is particularly preferable although any of these amine compounds can be used either singly or as a combination of two kinds or more according to need.

While additional addition of the above mentioned amine compound to the inventive photoresist composition may eventually have a disadvantageous effect of decreasing the photosensitivity of the composition, this disadvantage can be overcome, along with a beneficial effect of improving the pattern resolution, by the admixture of a carboxylic acid as a component (D) in combination with the component (C). Preferable carboxylic acids suitable for this purpose include aliphatic saturated dicarboxylic acids and aromatic carboxylic acids.

Examples of suitable aliphatic saturated dicarboxylic acids include oxalic, malonic, succinic and glutaric acids. Examples of suitable aromatic carboxylic acids include aromatic mono- and polycarboxylic acids having a hydroxyl or nitro group as a substituent group such as 2-hydroxy benzoic acid, 4-hydroxy benzoic acid, 2-hydroxy-3-nitro benzoic acid, 3,5-dinitro benzoic acid, 2-nitro benzoic acid, 2,4-dihydroxy benzoic acid, 2,5-dihydroxy benzoic acid, 2,6-dihydroxy benzoic acid, 3,4-dihydroxy benzoic acid, 3,5-dihydroxy benzoic acid, 2-vinyl benzoic acid, 4-vinyl benzoic acid, phthalic acid, terephthalic acid and isophthalic acid. These carboxylic acids can be used either singly or as a combination of two kinds or more according to need. Among the above named carboxylic acids, 2-hydroxy benzoic acid, i.e. salicylic acid, and malonic acid are particularly preferable.

As to the amount of the optional component (C) in the inventive photoresist composition, the amine compound is added to the composition in an amount in the range from 0.001 to 10 parts by weight or, preferably, from 0.01 to 1.0 part by weight per 100 parts by weight of the component (A). When the amount of the component (B) is too small, good pattern formation can hardly be accomplished while, when the amount of the component (B) is too large, a photoresist composition in the form of a uniform solution cannot be obtained due to the limited solubility of the component in an organic solvent to cause a decrease in storage stability of the photoresist solution.

While the essential ingredients in the inventive photoresist composition are the above described components (A) and (B), it is optional, if necessary with an object to improve orthogonality of the cross sectional profile of the patterned resist layer and stability of the latent images before development, that the photoresist composition further contains an aliphatic tertiary amine compound as a component (C). Examples of preferable aliphatic tertiary amine compounds include trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, triethanolamine, tributanol amine and the like, of which triethanolamine is particularly preferable although any of these amine compounds can be used either singly or as a combination of two kinds or more according to need.

While additional addition of the above mentioned amine compound to the inventive photoresist composition may eventually have a disadvantageous effect of decreasing the photosensitivity of the composition, this disadvantage can be overcome, along with a beneficial effect of improving the pattern resolution, by the admixture of a carboxylic acid as a component (D) in combination with the component (C). Preferable carboxylic acids suitable for this purpose include aliphatic saturated dicarboxylic acids and aromatic carboxylic acids.

Examples of suitable aliphatic saturated dicarboxylic acids include oxalic, malonic, succinic and glutaric acids. Examples of suitable aromatic carboxylic acids include aromatic mono- and polycarboxylic acids having a hydroxyl or nitro group as a substituent group such as 2-hydroxy benzoic acid, 4-hydroxy benzoic acid, 2-hydroxy-3-nitro benzoic acid, 3,5-dinitro benzoic acid, 2-nitro benzoic acid, 2,4-dihydroxy benzoic acid, 2,5-dihydroxy benzoic acid, 2,6-dihydroxy benzoic acid, 3,4-dihydroxy benzoic acid, 3,5-dihydroxy benzoic acid, 2-vinyl benzoic acid, 4-vinyl benzoic acid, phthalic acid, terephthalic acid and isophthalic acid. These carboxylic acids can be used either singly or as a combination of two kinds or more according to need. Among the above named carboxylic acids, 2-hydroxy benzoic acid, i.e. salicylic acid, and malonic acid are particularly preferable.

As to the amount of the optional component (C) in the inventive photoresist composition, the amine compound is added to the composition in an amount in the range from 0.001 to 10 parts by weight or, preferably, from 0.01 to 1.0 part by weight per 100 parts by weight of the component (A) in consideration of orthogonality of the cross sectional profile of the resist pattern, stability of the latent images before development and photosensitivity of the composition.

The amount of the carboxylic acid as the component (D), when added to the inventive photoresist composition, is in the range from 0.001 to 10 parts by weight or, preferably, from 0.01 to 1.0 part by weight per 100 parts by weight of the component (A). Addition of the component (D) to the

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US-PAT-NO: 5498765

DOCUMENT-IDENTIFIER: US

TITLE: Positive photoresist composition containing photoacid generator and use thereof

--------- KWIC --------

TITLE - TI (1):

Positive photoresist composition containing photoacid generator and use thereof

Abstract Text - ABTX (1):

A positive acting photoresist comprising a film forming reactive polymer; an iodonium initiator or a non-ionic compound that generates triflic acid upon exposure to radiation; and a multifunctional organic carboxylic acid is provided as well as use thereof.

Brief Summary Text - BSTX (3):

The present invention relates generally to mixtures of polymers and iodonium photoacid generators or non-ionic triflic acid generators used in resist compositions and, more specifically, to improved photoresist compositions for use in printed circuit board manufacture which function via an acid-catalyzed deprotection mechanism. More particularly, multifunctional organic carboxylic acids are employed in the compositions of the present invention to substantially reduce, if not entirely eliminate undevelopable resist and aid in the strippability of the resist.

Brief Summary Text - BSTX (5):

The design of chemically amplified resist systems based on acid-catalyzed chain reactions (e.g., polymerization, depolymerization, side chain- cleavage, etc.) has been recognized as a viable route to-high sensitivity resist systems in microlithography. Such systems are described in, e.g., Polymers In Electronics, Davidson T. Ed., ACS Symposium Series 242, American Chemical Society, Washington, D.C., 1984, page 11, H. Ito, C. G. Willson. These systems

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US005498765A

...ates Patent [19]

Carpenter, Jr. et al.

[11] Patent Number: 5,498,765

[45] Date of Patent: Mar. 12, 1996

[54] POSITIVE PHOTORESIST COMPOSITION CONTAINING PHOTOACID GENERATOR AND USE THEREOF

[75] Inventors: Burton J. Carpenter, Jr.; Michael G. Middlebrook; Joseph LaTorre, all of Austin, Tex.; Logan L. Simpson, Apalachin, N.Y.

[73] Assignee: International Business Machines Corporation, Armonk, N.Y.

[21] Appl. No.: 311,827

[22] Filed: Sep. 26, 1994

Related U.S. Application Data

[62] Division of Ser. No. 41,462, Apr. 2, 1993, Pat. No. 5,374,503.

[51] Int. Cl.[6] G03F 7/30; G03F 7/40

[52] U.S. Cl. 430/323; 430/326; 430/329

[58] Field of Search 430/323, 326, 430/329, 270, 910, 914, 919, 905, 277; 522/25, 26

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Primary Examiner—Jeffrey L. Dean

Attorney, Agent, or Firm—Pollock, Vande Sande & Priddy

[57] ABSTRACT

A positive acting photoresist comprising a film forming reactive polymer; an iodonium initiator or a non-ionic compound that generates triflic acid upon exposure to radiation; and a multifunctional organic carboxylic acid is provided as well as use thereof.

13 Claims, No Drawings

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